

Advances in Oil and Gas Exploration & Production

Neil Craigie

Principles of Elemental Chemostratigraphy

A Practical User Guide

 Springer

Advances in Oil and Gas Exploration & Production

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Preface

After spending several years studying towards B.Sc. (Hons) and M.Sc. degrees, I developed an interest in chemostratigraphy as I felt that ‘true’ innovation is most easily found at the borders of science. Chemostratigraphy may be loosely defined as a correlation technique involving the application of inorganic geochemical data, but this masks the fact that it involves elements of geochemistry, sedimentology and other disciplines. I was very fortunate to have been given the chance to work on a Ph.D. study in Chemostratigraphy at the University of Aberdeen from 1994 to 1998, under the supervision of Dr. Nigel Trewin and Dr. Malcolm Hole. At that time, very few publications existed on chemostratigraphy, and I gleaned much information through the painstaking process of trial and error.

After graduation, I worked as a geologist for an oil service company based in Croydon, Surrey, UK but I always yearned to apply the technique of chemostratigraphy in hydrocarbon reservoirs, rather than on the field outcrop sections I had been studying during my Ph.D. years. Finally, I got the opportunity to do this in the year 2000 when I joined Chemostrat Ltd., a small consultancy based in mid-Wales, UK. At that time, the company only employed four persons, but was in the process of expanding as they had signed an alliance agreement with Halliburton to develop a wellsite chemostratigraphy service. Not only was I able to work alongside Dr. Tim Pearce and Dr. Ken Ratcliffe (two of the Worlds leading experts on chemostratigraphy at that time) on conventional laboratory-based projects, I was also involved in the establishment of the first wellsite chemostratigraphy service. After working for Chemostrat Ltd. for 4 years, I was employed as a chemostratigrapher for Ichron Ltd. (2004–2012) and then Saudi Aramco (2012–present). I have watched chemostratigraphy grow in stature and popularity from 1994 to present, exemplified by a sharp increase in the number of publications from 2009. The level of interest is also shown by a rise in the number of companies offering chemostratigraphy as a service. In the late 1990s, for instance, nearly all chemostratigraphy projects were completed by only two oil service companies—Chemostrat Ltd. and IRES Ltd, both being based in the UK. At the time of writing, the list of companies undertaking Chemostratigraphy projects include Chemostrat Ltd., IRES Ltd., Weatherford, Halliburton, Schlumberger, CGG, RPS Ichron, Stratochem and others.

Despite this meteoric growth in popularity, very few, if any, publications provide detailed information on sampling, sample preparation, analytical techniques and interpretive methodologies. Instead, most describe the final results and interpretations in depth without explaining how they were achieved. Similarly, very few papers describe any of the multitude of potential pitfalls associated with each step of a chemostratigraphy study, from the sampling of core/cuttings to interpreting data. Chemostratigraphy is almost never taught at undergraduate level, making it very difficult for students to acquire a sufficient level of knowledge on the subject. Though some companies offer formal training in chemostratigraphy, they do not, as a general rule, make these courses available to individuals working outwith the company.

I take a pragmatic long-term view that the only way the subject will develop as a whole will be for this information to be released to the wider geological community. Having taught chemostratigraphy to many young professionals, the following question often crops up—‘where can I find a textbook detailing the methodologies and information I require in order to become a chemostratigrapher?’ Up until now, it is my opinion that no such textbook exists. It is hoped that this book will inspire young professionals and others to take an interest in the subject.

Dhahran, Saudi Arabia

Neil Craigie

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I would like to thank several former work colleagues at RPS Ichon including Michael Leeds, Benjamin Lee and Daniel Atkin. The many hours we spent discussing the intricacies of reservoir correlation, and time we endured on oil rigs working on wellsite chemostratigraphy studies, were truly inspirational. Gratitude should go to former colleagues at Chemostrat Ltd., including Tim Pearce, Ken Ratcliffe and John Martin. Much of my knowledge in chemostratigraphy was gained from working with these individuals in the early 2000s. I completed my Ph.D. in chemostratigraphy at the University of Aberdeen in 1998 and would like to take this opportunity to thank my supervisors, Nigel Trewin and Malcolm Hole. I will never forget the advice and training they gave me from 1994 to 1998, and they are, at least in part, responsible for inspiring me to form a career in chemostratigraphy.

Last but by no means least, I would like to thank my wife Kathryn Craigie and my daughter Iona Craigie. They have had to get used to my absences during the many evenings and weekends spent writing this book, but have remained supportive throughout this process.

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Abstract

Chemostratigraphy may be defined as a correlation technique involving the application of inorganic geochemical data. It has become very popular as a hydrocarbon reservoir correlation tool over that last 20 years, mainly owing to improvements in analytical techniques, as it is now possible to analyze core, cuttings and field outcrop samples with a degree of efficiency that was not possible prior in the 1970's and 1980s. The advantages of chemostratigraphy are that it can be applied to sediments of any lithology, any age, found in any location and deposited in any environment. In addition to this, it may be utilized on core, sidewall core, cuttings and field outcrop samples, with an equal degree of ease. Perhaps the greatest benefit of chemostratigraphy, however, is that it offers a higher level of resolution than most other techniques. Using ICP (Inductively Coupled Plasma) and XRF (X-Ray Fluorescence) technologies, it is possible to acquire good quality data for around 55 and 42 elements respectively, in the range Na-U in the periodic table. This results in at least 42 potential variables that can be used for chemostratigraphic characterization and correlation. In fact, the number often exceeds 250 when elemental ratios are taken into account. The high levels of resolution are also explained by the low limits of detection of analytical instruments. Using modern XRF spectrometers it is possible to measure the abundances of most elements in concentrations of 1 ppm or less and, given that 1wt % is approximately equivalent to 10,000 ppm, it is obvious that minor changes in mineralogy and geochemistry can be recorded. The ICP technique offers even better levels of resolution/detection, with some trace elements and REE recorded at levels of less than 1 ppb. Consequently, very subtle changes in the mineralogy, such as variations in the distribution of specific heavy minerals and other accessory minerals occurring in the region of 0.1–2%, can be modeled using whole rock geochemical data. In spite of the aforementioned benefits of using chemostratigraphy as a reservoir correlation tool, numerous 'pitfalls' exist at every stage of a chemostratigraphy project. The study is likely to fail, for instance, if the sampling strategy is inadequate, or if cuttings samples have not been washed prior to analysis. An inability of the chemostratigrapher to

recognize poor quality data or analytical drift are also potential reasons for failure. In addition to this, a number of challenges are associated with the interpretation of inorganic geochemical data and the proposition of correlation schemes. It is hoped that the information outlined in the following chapters will serve as a ‘step-by-step’ guide to chemostratigraphy and inspire the next generation of chemostratigraphers to further develop the technique.

1.1 Development of Elemental Chemostratigraphy

The definition of chemostratigraphy is stated as “the study of the chemical variations within sedimentary sequences to determine stratigraphic relationships” (<https://en.wikipedia.org/wiki/Chemostratigraphy>). However, this definition in the Wikipedia website may be slightly misleading as the technique can also be used as a stratigraphic aid in igneous rocks (Ramkumar 2015). Nevertheless, given that nearly every chemostratigraphy study is performed on sediments or sedimentary rocks, the application of the technique in other rock types is not covered in the present book.

The subject of chemostratigraphy can be broadly subdivided into isotope and elemental chemostratigraphy (Ramkumar 2015; Sial et al. 2015), but the present publication focuses on the latter. The applications of isotopes in chemostratigraphy would warrant the publication of a separate book but, for detailed information on this, the reader is referred to the excellent works of Veizer et al. (1980), Lindsay and Brasier (2002), Calver et al. (2004), Kaufman et al. (2007), Allen and Etienne (2008), Saltzman and Thomas (2012), Sial et al. (2015) and others. In the same way that biostratigraphy was ‘morphed’ into the subfields of palynology, micropaleontology and nanopaleontology, it is felt that chemostratigraphy has developed to such an extent that it should be viewed in terms of two distinct sub-categories: elemental and isotope chemostratigraphy. Much of the information presented in the following chapters relates to the application of elemental chemostratigraphy to

correlate hydrocarbon-bearing reservoirs, but its use is certainly not restricted to the petroleum sector as methodologies are equally applicable to non-reservoir intervals, including field outcrop studies.

Chemostratigraphy was pioneered in the 1970s but few papers were published until the 1980s (e.g. Kishida and Riccio 1980; Zhengyong et al. 1985; Vuorinen et al. 1986) and early 1990s (e.g. Pearce and Jarvis 1991; MacLean and Barret 1993). In a recent search of chemostratigraphy publications in www.sciencedirect.com (detailing works published by Elsevier), the author found only 178 articles from before 1997 (of which most were written after 1992) and less than 340 articles per year were published from 1998 to 2003. A total of only 53, 31 and 40 articles were published in 2005, 2006 and 2007 respectively, whilst the number increased to the range 63–84 from 2007–2012. This number exceeded 100 per annum in the period 2013–2016. Similar increases in the number of chemostratigraphy related articles have been recorded on other websites such as www.GeoscienceWorld.org, and www.Springerlink.com (Ramkumar 2015). Note that these figures are based on articles published on both elemental and isotope chemostratigraphy but, a cursory examination of titles and abstracts revealed the number of articles written in both subjects have increased exponentially over the years. Provision of a full list of papers published on elemental chemostratigraphy is beyond the scope of the present study, but some of the more noteworthy contributions are Pearce and Jarvis (1991), Pearce et al. (1999, 2005), Ratcliffe et al. (2006), Davies et al. (2013), Sano et al. (2013), Holmes et al. (2015), Madhavaraju et al. (2015),

Ramkumar (2015), Craigie (2015a, b), Craigie et al. (2016a, b), and Craigie and Polo (2017).

Other signs of the increase in popularity of chemostratigraphy are obvious to persons involved in the petroleum sector. Prior to 1992, nearly all chemostratigraphy work was completed by only two companies—Geochem Group Ltd, and Kingston Geological Services Ltd. From 1993 to 1999, the companies Chemostrat Ltd and IRES Ltd became the leading providers of this service. It is noteworthy, however, that these four companies were based entirely in the UK and, though they completed some international studies, much of their work was focused on projects in the North Sea region. Since that time, the number of companies involved in chemostratigraphy have increased sharply and now include Chemostrat Ltd, RPS Ichron, CGG, Halliburton, Schlumberger, Baker Hughes, IRES, StratoChem and others. Most of these companies complete studies throughout the globe and some have five or more regional offices. It is also apparent that at least some companies have witnessed a sharp increase in the number of staff that they employ in this field. For example, Chemostrat Ltd only employed 4 persons when the author joined the company in the year 2000, but employed around 100 by 2015 (Dr Tim Pearce, Director of Chemostrat Ltd—personal communication). Many oil companies also see the benefit of chemostratigraphy and employ specialists in this field.

The reasons for this increase may be manifold but arguably the main ‘driver’ involved improvements in analytical technology. ICP (Inductively Coupled Plasma) and XRF (X-ray Fluorescence) instruments are now capable of acquiring data for more than 40 elements in a very short timeframe. Furthermore, levels of analytical accuracy (closeness of result to a known value), precision (i.e. repeatability of results) and detection limits (typically 1 ppm by XRF and 1 ppb by ICP) have improved over the years. Related to this is the development of benchtop XRF spectrometers that became small and robust enough to be utilized at wellsite where data could be acquired in ‘near real time’. This service was first introduced by the Chemostrat:

Halliburton business alliance in the early 2000s but was then followed by IRES Ltd, RPS Ichron, Schlumberger and others. Another factor contributing to the popularity of chemostratigraphy may relate to improvements in software applications since the early 1990s. Prior to this time it would have taken much longer to achieve relatively simple tasks such as plotting profiles for individual elements, or creating binary diagrams, and some of this work may have had to be done by hand. With the advent of industry-standard applications such as ODM (Oilfield Data Manager), IC, Petrel and others, however, these tasks became much easier to accomplish. Ramkumar (2015) cites the economic liberalization in many countries following the end of the Cold War in the late 1980s to early 1990s as a possible explanation for the increase in usage of chemostratigraphy. According to Ramkumar (2015) “the end of the Cold War has heightened the energy demand that in turn necessitated hydrocarbon exploration in areas hitherto remained unexplored and/or less explored. The petroleum sector has clearly benefited from the development of chemostratigraphy as a reservoir correlation tool, enabling oil companies to produce improved exploration and development strategies.”

In spite of the increase in popularity, chemostratigraphy is hardly ever taught at undergraduate level in universities and colleges and surprisingly little information has been published on methodologies relating to sampling, sample preparation/analysis and the interpretation of data. For instance, most papers illustrate details the ‘final’ chemostratigraphic scheme proposed by the author(s) but very few explain why certain key element/ratios were used instead of others, how the mineralogical affinities of elements were established, how the samples were selected and then prepared prior to analysis, or how data quality was measured. There is an almost non-existence of courses provided to the wider geological community on chemostratigraphy by oil service companies and academic institutions alike.

The author believes that the subject of chemostratigraphy can only grow and develop

through the sharing of information. Perhaps the most appropriate analogies are in the fields of sedimentology and biostratigraphy, where the publication of textbooks has resulted in the flow of knowledge between academic institutions and companies alike, leading to the inspiration of many students to form careers in these subjects. In contrast to both sedimentology and biostratigraphy, very few geologists graduate from universities as specialists in chemostratigraphy. The route that most chemostratigraphers have taken were to join oil service companies as BSc, MSc or PHD graduates, and then to either learn the subject through the process of ‘trial and error’ or be provided with more formal training.

Many papers have been written on chemostratigraphy, yet the author only found one book dedicated entirely to the study of the science—a publication by Ramkumar (2015). This commences with a brief introduction to the technique of chemostratigraphy (Ramkumar 2015), followed by a series of articles written about on the applications of both elemental and isotope chemostratigraphy in specific field outcrop localities throughout the globe (e.g. Madhavaraju et al. 2015; Morath et al. 2015; Sial et al. 2015). One unfortunate aspect of this book is that these articles are written about different case studies and provide very little information on methodologies. The present book is intended to take the form of a comprehensive users guide to elemental chemostratigraphy, detailing all stages of a chemostratigraphy study from sampling to proposing a chemostratigraphic correlation scheme. It is believed to be the first of its kind to provide such an in depth step-by-step guide to chemostratigraphy, and it is hoped that this will inspire more graduates to form a career and the subject and to develop it as a science in the future.

1.2 Applications and Pitfalls

The obvious advantages of elemental chemostratigraphy are that it can be utilized in sediments of any lithology, any age, found in any location and deposited in any environment. This

does not hold true for many other the disciplines. Biostratigraphy, for instance, often works best on mudrocks and siltstones deposited in suboxic-anoxic paleoenvironments. Conventional heavy mineral analysis is a commonly used technique to correlate reservoirs, but is normally only applied on the sand fraction.

A further advantage of the technique is that it can be applied to field outcrop, core, sidewall core and ditch cuttings samples with an equal degree of success. Some other techniques, such as petrography and heavy mineral analysis nearly always work far better on core than on cuttings. Perhaps the greatest advantage of chemostratigraphy, however, is that it offers a higher level of resolution than other techniques. Using ICP and XRF technologies, it is possible to acquire good quality data for around 55 and 42 elements respectively, in the range Na-U in the periodic table. This means that 42 or more variables could be used for the purpose of chemostratigraphic characterization and correlation. In reality the number is far greater than that and exceeds 300 variables when elemental ratios are taken into account. This differs from the more traditional XRD (X-Ray Diffraction) and petrography techniques where the number of variables are normally restricted to less than 15. Similarly, many schemes are based on trends in wireline logs but these do not normally number more than 12 in most wells.

Chemostratigraphy also hold the advantage that incredibly high levels of resolution are achieved by analytical instruments. Using modern XRF spectrometers it is possible to measure the abundances of most elements in concentrations of 1 ppm or less and, given that 1% is equivalent to 10,000 ppm, it is obvious that very subtle changes in mineralogy and geochemistry can be recorded. The ICP technique offers even better levels of resolution/detection, with some trace elements and REE (Rare Earth Elements) recorded at levels of less than 1 ppb. Consequently, very subtle changes in the mineralogy, such as variations in the distribution of specific heavy minerals and other accessory minerals in the region of 0.1–2% can be modeled using geochemical data. By contrast, when applying a

standard 'point count' of 300 per slide, it is normally only possible to use petrographic data to recognize changes of 10% or more in the concentration of these minerals. For these reasons, elemental chemostratigraphy offers unique levels of versatility and resolution which cannot be achieved using other techniques.

It is unfortunate that the popularity of the technique and general lack of information on methodologies has resulted in many examples of malpractice, which the author believes has resulted in the private criticism of the technique vented by a small number of individuals working for oil/service companies, and by the public criticism of the technique on the part of academics (e.g. North et al. 2005; Hurst and Morton 2014). The failure of many studies can be traced to inadequate sampling and sampling preparation techniques. For example, a simple failure to wash cuttings to remove drilling additives, the incorrect 'picking' of ditch cutting cuttings to ensure good 'representivity', or failure to grind core/cuttings samples properly can result in the acquisition of poor quality data that cannot be utilized for subsequent chemostratigraphic purposes. Other failures occur during data generation and may relate to the inability of interpreters to recognize good and poor quality data. For example, analytical drift may be identified by analyzing standard reference on a frequent basis, but may never be recognized if these samples are not run in the first instance. Without good quality data, it is almost impossible to produce a chemostratigraphic scheme with any confidence. Sampling, sample preparation procedures, analytical techniques and the quality control of data are covered in Chap. 2 of this book.

In addition of the acquisition of data, there are many challenges in the interpretation of geochemical data. Many inexperienced chemostratigraphers produce schemes without gaining an understanding of the mineralogical affinities of the elements they are using for chemostratigraphic purposes. This should be achieved by comparing geochemical data with mineralogical

data derived from XRD, petrographic and/or heavy mineral analysis. It is also important to use statistical and graphical techniques for this purpose. The techniques used to establish element: mineral links and the controls on geochemistry and mineralogy are described in detail in Chap. 3. This section also provides more general information on the geochemistry of minerals that are most likely to be encountered in clastic and carbonate sedimentary rocks.

A common fault made by many inexperienced chemostratigraphers is to interpret profiles plotted for elements and ratios in the same way they would for wireline log data. A pronounced upward increase in the GR (Gamma Ray) profile, for instance, may signify a decrease in grain size and be used for inter-well correlation purposes. Applying the same philosophy to geochemical data can be problematic, however, where a trend may be based on a small number of samples yielding local increases in elements that only exist in the immediate vicinity of the given well and cannot be used for correlation. Failure to take into account variations in grain size, carbonate dilution are other factors may also result in erroneous correlations. The techniques used to interpret data and the many pitfalls relating to the interpretation of data are discussed in Chap. 4.

Chapter 5 of this book explains how chemostratigraphy can be applied to the correlation of carbonate, clastic and unconventional (source rock) reservoirs. A more recent development in chemostratigraphy has been to use the technique as part of a multidisciplinary approach to reservoir correlation. The use of chemostratigraphy, in conjunction with reservoir sedimentology and biostratigraphy has obvious advantages, namely it is possible to produce schemes that are more detailed and confident. Most chemostratigraphic schemes are based on the recognition of changes in provenance, reflected by changes in the chemistry and abundance of detrital minerals. These changes in provenance are normally time-equivalent on a

field scale between closely spaced wells (i.e. where wells are less than 10 miles apart), but this does not always hold true on a larger subregional-regional scale, where the same chemostratigraphic units can be deposited in different stratigraphic intervals at different times. This diachroneity can be modeled where biostratigraphic, sedimentological and seismic data are used in conjunction with chemostratigraphy. This inevitably means that the chemostratigrapher should be a good all round geologist with a basic knowledge of reservoir sedimentology, biostratigraphy, seismic interpretation, borehole image techniques and others. The importance of employing such an integrated approach to reservoir correlation is illustrated by some of the case studies presented in this chapter. Chemostratigraphy is increasing used in unconventional (source rock) reservoirs where the objectives are often twofold—to provide a chemostratigraphic scheme, and to use the inorganic geochemical data to model variations in unconventional reservoir properties such as TOC (Total Organic Carbon), clay abundance and brittleness. This subject is also covered in Chap. 5.

Chapter 6 discusses the applications of chemostratigraphy at wellsite. This has been in operation since the early 2000's but very few papers have been published on the subject and most take the form of short conference abstracts. Furthermore, very little, if any, information has been published on the unique challenges faced by the wellsite chemostratigrapher. Though most of the sampling, sample preparation, analytical and data interpretation procedures are applicable to both wellsite and conventional/laboratory based studies, the former presents additional challenges, many of which relate to the necessity for the wellsite chemostratigrapher to work at speed and often under considerable pressure. Adaptation of these procedures is often necessary, as is an ability to communicate with numerous members of staff working on the rig during the duration of drilling. For example, it is

important for the chemostratigrapher to converse with the mud engineer to find out the type and quantity of drilling additives to be used and whether this will change during the drilling of the given well. The failure of at least some wellsite chemostratigraphy studies are traced back to a simple lack of communication on the part of the wellsite chemostratigrapher(s). Most of the information presented in the chapter has not been published previously and is based entirely on the authors experience of assisting in the development of the first wellsite chemostratigraphy services, and of working at wellsite during the drilling of numerous wells from the years 2004 to 2012.

1.3 Standardization of Terminology

One frustrating aspect of chemostratigraphy as a subject (both elemental and isotope chemostratigraphy) is that it has been developed in slightly different ways by separate individuals and companies, with terms never having been formally defined or universally accepted. Ramkumar (2015) describes a chemozone as “the unique rock record defined by chemostratigraphic indices and recognizable through unique geochemical signature(s) which in turn helps distinction of a designated rock record from other rock records and also correlation with applicable analogs at appropriate/applicable spatiotemporal scale.” The author agrees with this definition and uses it as a general term to describe any unit or zone that has a unique geochemical signature in a given study section. Other authors use different terminologies. For example Montero-Serrano et al. (2010) use the term “chemofacies” which is understood to be synonymous with “chemozone”. However, the word “chemofacies” may be slightly confusing as it may infer that chemozones reflect changes in depositional environment, which is often not the case. Sano et al. (2013), use the terms ‘packages’ and ‘units’.

There is not particular problem with using this terminology, except that some confusion may occur as these are also used in sequence stratigraphy studies. The author prefers to use the following terms in decreasing hierarchical order:

Zones

Subzones

Divisions

Subdivisions

Rarely is it necessary to produce more than 4 orders of hierarchy, but the terms ‘units’, ‘sub-units’ and ‘beds’ could be introduced if it is. For further information on the use and misuse of terminology relating to chemostratigraphy projects, the reader is referred to the publication of Ramkumar (2015). That fact that many of the terms mentioned by this author have not been universally accepted/applied, and are used in different context by different workers, led the author of the present book to provide no further discussion on this subject. Ultimately, the terms used in chemostratigraphy studies should be of much less importance than adoption of the correct methodologies to the interpretation of inorganic geochemical data.

1.4 The Future of Chemostratigraphy

As with the development of chemostratigraphy from the 1970’s to present, it is highly probably that future advancements will be driven by improvements in analytical technology. ICP, XRF and other analytical instruments are becoming smaller, easier to use, more robust with time, and significant improvements have also been made to the speed and quality of data acquisition. Further enhancement may take the form of much smaller instruments available at lower price tags, thus encouraging more companies, academic institutions and individuals alike to take an interest in the technique. It is also believed, however, that the development of chemostratigraphy as a science can only happen if

there is a greater willingness on the part of these groups to share information, including innovative interpretation techniques. It is hoped that the following chapters will go some way to improving the availability of information on the subject of elemental chemostratigraphy and may inspire the next generation of chemostratigraphers.

References

- Allen, P.A., & Etienne, J.L. (2008). Sedimentary challenge to Snowball Earth. *Nature Geoscience*, 1(12): 817–825.
- Calver, C.R., Black, L.P., Everard, J.L., & Seymour, D.B. (2004). U-Pb zircon age constraints in late Neoproterozoic glaciation in Tasmania. *Geology*, 32, 892–896.
- Craigie, N. W. (2015a). Applications of chemostratigraphy in cretaceous sediments encountered in the North Central Rub’ al-Khali Basin, Saudi Arabia. *Journal of African Earth Sciences*, 104, 27–42.
- Craigie, N. W. (2015b). Applications of chemostratigraphy in middle Jurassic unconventional reservoirs in eastern Saudi Arabia. *GeoArabia*, 20(2), 79–110.
- Craigie, N. W., Breuer, P., & Khidir, A. (2016a). Chemostratigraphy and biostratigraphy of Devonian, Carboniferous and Permian sediments encountered in eastern Saudi Arabia: An integrated approach to reservoir correlation. *Marine and Petroleum Geology*, 72, 156–178.
- Craigie, N. W., Rees, A., MacPherson, K., & Berman, S. (2016b). Chemostratigraphy of the Ordovician Sarah Formation, North West Saudi Arabia: An integrated approach to reservoir correlation. *Marine and Petroleum Geology*, 77, 1056–1080.
- Craigie, N. W., & Polo, C. A. (2017). *Applications of chemostratigraphy and sedimentology in a complex reservoir: A case study from the Permo-Carboniferous Unayzah group*. Central Saudi Arabia: Marine and Petroleum Geology (in prep.).
- Davies, E. J., Ratcliffe, K. T., Montgomery, P., Pomar, L., Ellwood, B. B., & Wray, D. S. (2013). *Magnetic susceptibility (X stratigraphy) and chemostratigraphy applied to an isolated carbonate platform reef complex; Lluçmajor Platform, Mallorca*. SEPM Special Publication dedicated to the deposits, architecture and controls of carbonate margin, slope and basin systems.
- Holmes, N., Atkin, D., Mahdi, S., & Ayress, M. (2015). Integrated biostratigraphy and chemical stratigraphy in the development of a reservoir-scale stratigraphic framework for the Sea Lion Field area, North Falkland Basin. *Petroleum Geoscience*, 21, 171–182.
- Hurst, A., & Morton, A. (2014). Provenance models: The role of sandstone mineral-chemical stratigraphy. In R. A. Scott, H. R. Smyth, A. C. Morton, & N. Richardson (Eds.) (Vol. 386, pp. 7–26). Geological Society Special Publications.

- Kaufman, A.J., Sial, A.N., & Ferreira, V.P. (2007). Preface to Special Issue of Chemical Geology on Precambrian Chemostratigraphy in honor of the late William T. Holsler. *Chemical Geology*, 237(1-2): 1–4.
- Kishida, A., & Riccio, L. (1980). Chemostratigraphy of lava sequences from the Rio Itapicuru Greenstone Belt, Bahia State, Brazil. *Precambrian Research*, 1(2), 161–178.
- Lindsay, J. F., & Brasier, M. D. (2000). A carbon isotope reference curve for ca. 1700–1575 Ma, McArthur and Mount Isa Basins, Northern Australia. *Precambrian Research*, 99(3), 271–308.
- Maclean, W. H., & Barrett, T. J. (1993). Lithochemical techniques using immobile elements. *Journal of Geochemical Exploration*, 48, 109–133.
- Madhavaraju, J., Hussain, S. M., Ugeswan, J., Nagarajan, R., Ramasamy, S., & Mahalakshmi, P. (2015). Paleo-redox conditions of the Albian-Danian carbonate rocks of the Cauvery Basin, south India: Implications for chemostratigraphy. In Ramkumar M (Ed.), *Chemostratigraphy—Concepts, techniques and application* (pp. 247–271). Amsterdam: Elsevier.
- Montero-Serrano, J. C., Palarea-Albaladejo, J., Martin-Fernandez, J. A., Martinez-Santana, M., & Guitierrez-Martin, J. V. (2010). Sedimentary chemo-facies characterization by means of multivariate analysis. *Sedimentary Geology*, 228, 218–228.
- Morath, P., Carvert, L., & White, T. (2015). A chemostratigraphic model for the development of parasequences and its application to sequence stratigraphy and paleoceanography, Cretaceous Western Interior Basin, USA. In M. Ramkumar (Ed.), *Chemostratigraphy—Concepts, techniques, and applications* (Chap. 9, pp. 215–246). Amsterdam: Elsevier.
- North, C. P., Hole, M. J., & Jones, D. G. (2005). Geochemical correlation in deltaic successions: A reality check. *Geological Society of America Bulletin*, 117(5/6), 620–632.
- Pearce, T. J., & Jarvis, I. (1991). Applications of geochemical data to modeling sediment dispersal patterns in distal turbidites: Late quaternary of the Madeira abyssal plain. *Journal of Sedimentary Petrology*, 62, 1112–1129.
- Pearce, T. L., Besley, B. M., & Wray, D. S. (1999). Chemostratigraphy: A method to improve interwell correlation in barren sequences—A case study using onshore Duckmantian/Stephanian sequences (West Midlands, UK). *Sedimentary Geology*, 124, 197–220.
- Pearce, T. J., Wray, D. S., Ratcliffe, K. T., Wright, D. K., & Moscardiella, A. (2005). Chemostratigraphy of the upper carboniferous schooner formation, southern North Sea. In J. D. Colinson, D. J. Evans, D. W. Holiday, & N. S. Jones (Eds.), *Carboniferous hydrocarbon geology: The southern North Sea and surrounding onshore areas* (Vol. 7, pp. 147–164). Yorkshire Geological Society, Occasional Publication Series.
- Ramkumar, M. (2015). Toward standardization of terminologies and recognition of chemostratigraphy as a formal stratigraphic method. In M. Ramkumar (Ed.), *Chemostratigraphy—Concepts, techniques, and applications* (Chap. 1, pp. 1–22). Amsterdam: Elsevier.
- Ratcliffe, K. T., Martin, J., Pearce, T. J., Hughes, A. D., Lawton, D. E., Wray, D. S., et al. (2006). A regional chemostratigraphically-defined correlation framework for the Late Triassic TAG-I Formation in Blocks 402 and 405a, Algeria. *Petroleum Geoscience*, 12, 3–12.
- Sano, J. L., Ratcliffe K. T., & Spain, D. (2013). Chemostratigraphy of the Haynesville Shale. In U. Hammes & J. Gale (Eds.), *Geology of the Haynesville gas shale in East Texas and West Louisiana, USA. AAPG Memoir 105*, 137–154.
- Saltzman, M.R., & Thomas, E. (2012). Carbon isotope stratigraphy. In F. M. Gradstein, J. G. Ogg, M. Schmitz, & G. Ogg (Eds.), *The Geological Time Scale*. Elsevier <http://dx.doi.org/10.1016/B978-0-444-59425-9.00011-1>
- Sial, A. N., Gaucher, C., Ferreira, V. P., Pereira, N. S., Cezario, W. S., Chigliano, L., & Lima, H. M. (2015). Isotope and elemental chemostratigraphy. In M. Ramkumar (Ed.), *Chemostratigraphy—Concepts, techniques, and applications* (Chap. 2, pp. 23–64). Amsterdam: Elsevier.
- Veizer, J., Holsler, W.T., & Wilgus, C.K., 1980. Correlation of $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$ secular variations. *Geochimica et Cosmochimica Acta*, V. 44, pp. 579–588.
- Vuorinen, A., Alhonen, P., & Suksi, J. (1986). Palaeolimnological and limnogeochimical features in the sedimentary record of the polluted Lake Lippajarvi in Southern Finland. *Environmental Pollution Series A, Ecological and Biological*, 41, 323–362.
- Zhengyong, Q., Xiuen, Y., & Mingmei, J. (1985). Chemostratigraphic correlation of the middle and upper Proterozoic between the Yanshan and Shennongjia Basin. *Precambrian Research*, V. 29(1–3), 55–91.

Abstract

Very little information has been published on sampling and sample preparation procedures, yet these are paramount to the success of chemostratigraphy as, without good quality data, it is not possible to produce robust chemostratigraphic schemes. This is especially true of studies involving the analysis of cuttings samples, which have to be washed, sieved, meticulously ‘picked’ and ground prior to analysis. Core and field outcrop samples are simply described and then ground. The principal analytical techniques used to acquire inorganic geochemical data are ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry), ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) and XRF (X-ray Fluorescence). For the best quality data acquired for the largest number of elements, it is recommended that a combination of ICP-OES and ICP-MS are used. The XRF technique produces data for a lesser number of elements, but can be useful where rapid analysis of samples is required. Irrespective of the analytical technique used to acquire data, however, it is important to check the results for accuracy (closeness of result to ‘known’ values of particular elements), precision (repeatability of results) and detection limits, before the data can be utilized for chemostratigraphic purposes.

2.1 Introduction

The following chapter commences with information on sampling strategies and sample preparation techniques, followed by an outline of the principal analytical techniques used in chemostratigraphy studies. A discussion on data quality assessment is included towards the end of the chapter. Much of the information on

sampling and sample preparation has not been published in any detail, hence the lack of referenced works on these subjects. Some publications include information on sample preparation and analytical procedures (e.g. Pearce et al. 2005; Craigie 2015a; Craigie 2015b; Madhavaraju 2015), but this is often summarized and lacking in detail. In spite of this, sample preparation and analytical procedures are considered by the